HETEROGENEOUS AZEOTROPIC DEHYDRATION OF ETHANOL TO OBTAIN A CYCLOHEXANE-ETHANOL MIXTURE

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OBJECTIVE

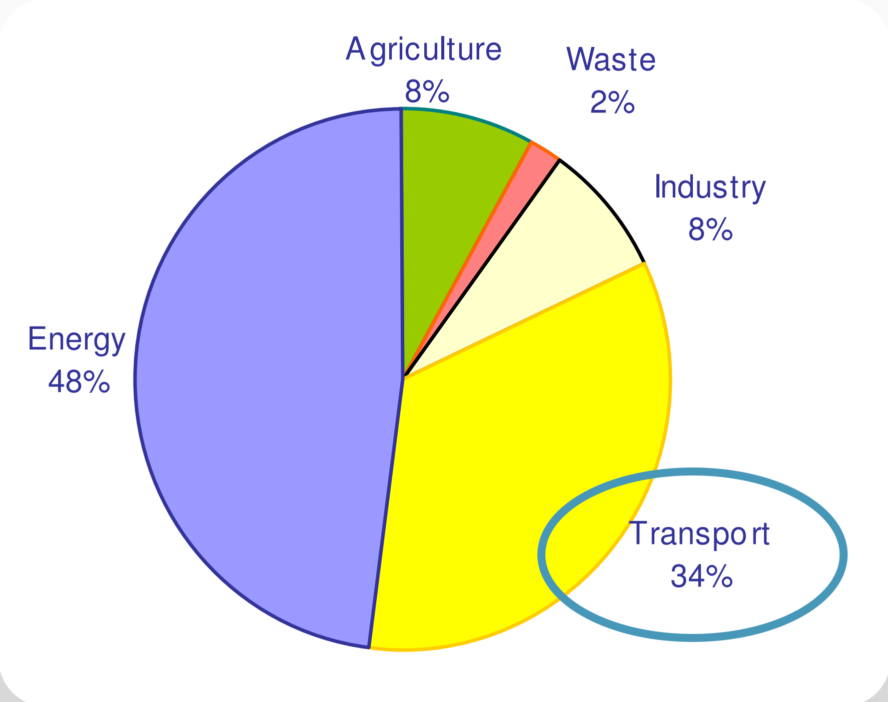
Study the viability of cyclohexane in the ethanol dehydration to obtain an **ethanol + cyclohexane mixture** from an azeotropic distillation column.

Key renewable energy policy documents of the EU

- **1997 White Paper "Energy for the future"**
  - Doubling the share of renewable energy from 6% (1997) to 12% (2010)
- **2003 EU Biofuels Directive (2003/30/EC)**
  - Target for biofuels in transport: 2% by 2005, 5.75% by 2010
- **2009 Directive „on the promotion of the use of energy from renewable sources“ (2009/28/EC)**
  - Overall EU target : 20% renewable energy in gross final energy consumption in 2020
  - Target of 10% renewable energy in transport in 2020 for all member states

Ethanol Production

Sectored emissions in Europe

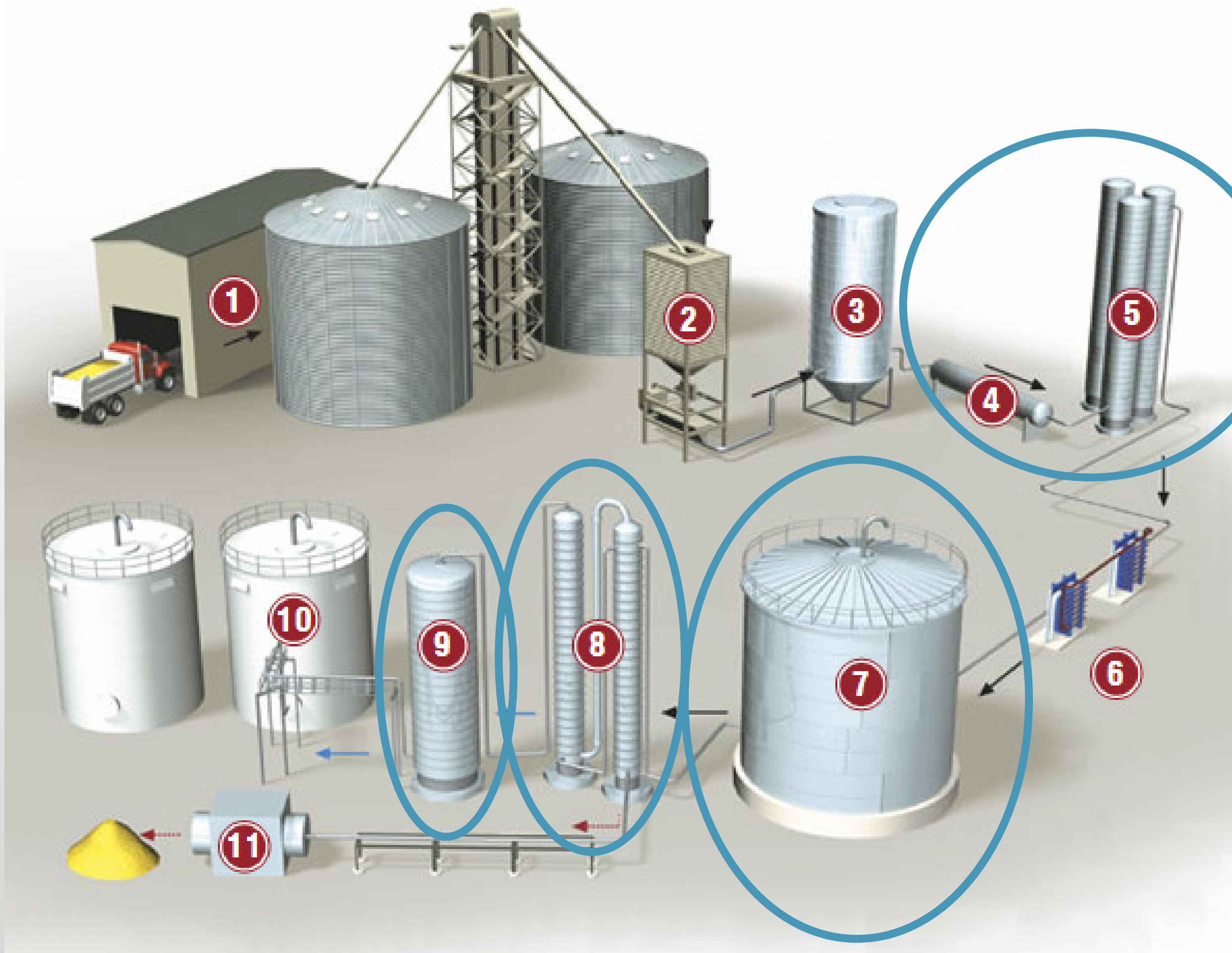


Benefits of biofuels

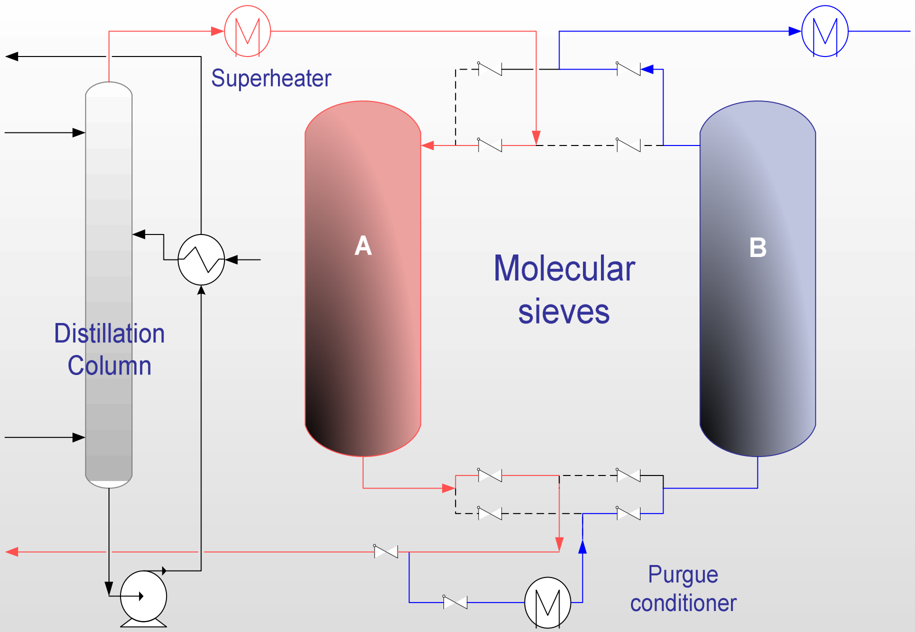
- Reduce GHG emissions
- Improve air quality
- Reduce petroleum dependence
- Improve energy security

Ethanol Production

1. Unloading
2. Milling
3. Mashing
4. Cooking
5. Hydrolysis
6. Cooling
7. Fermentation
8. Distillation
9. Dehydration
10. Storage
11. Stillage treatment



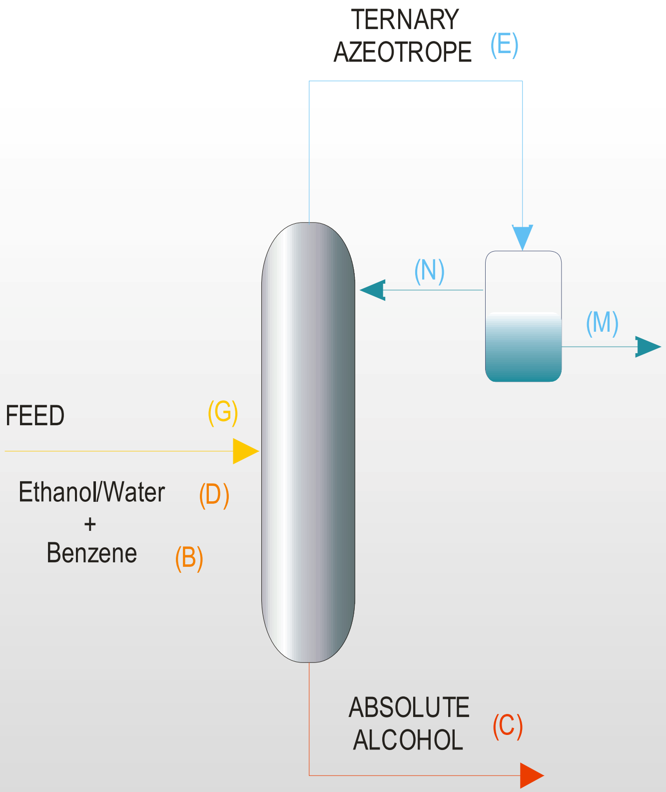
Ethanol dehydration

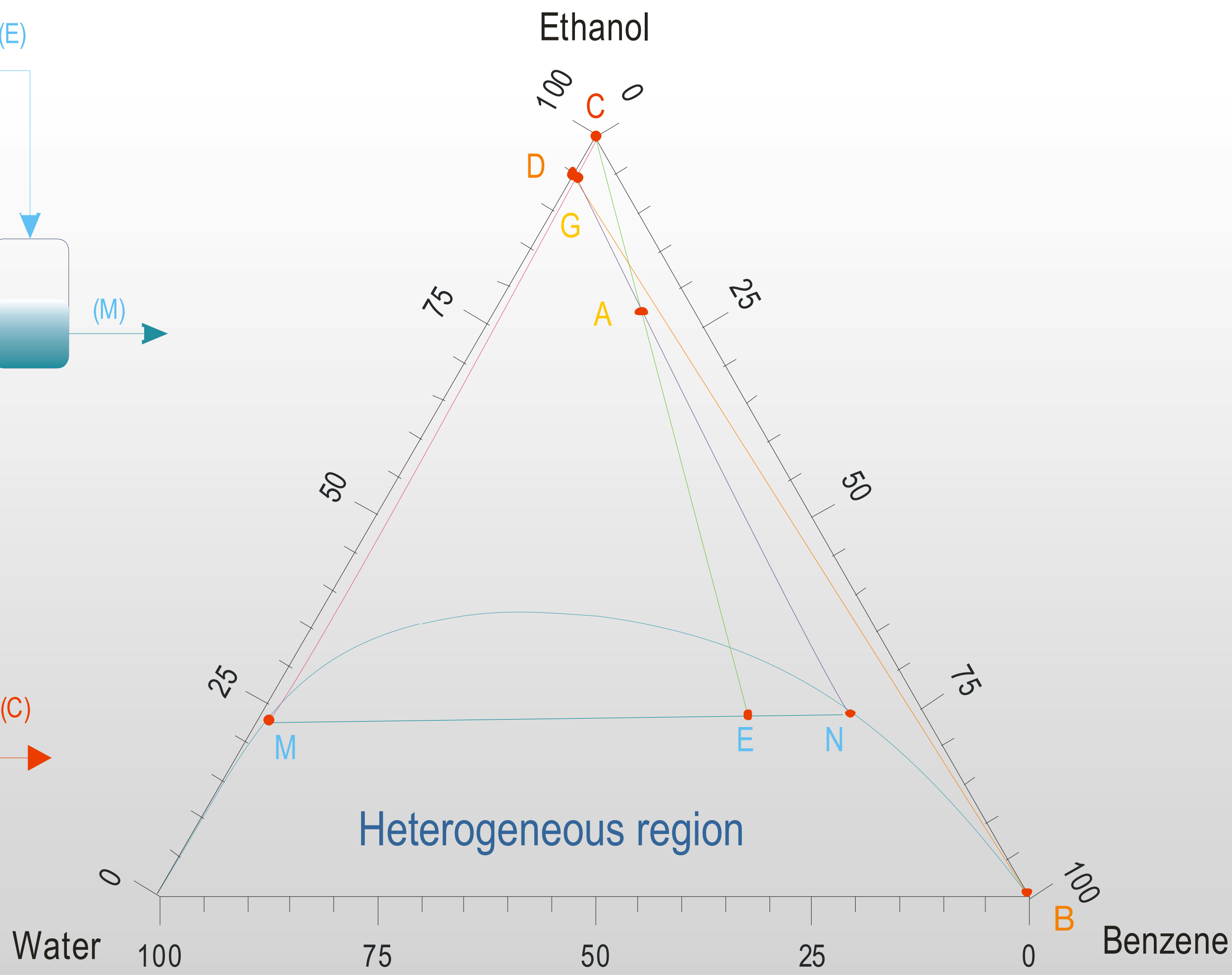


Pressure Swing Adsorption

Azeotropic distillation

Azeotropic distillation





Possible entrainers

Benzene ( )

Pentane

Acetone

Hexane

Heptane

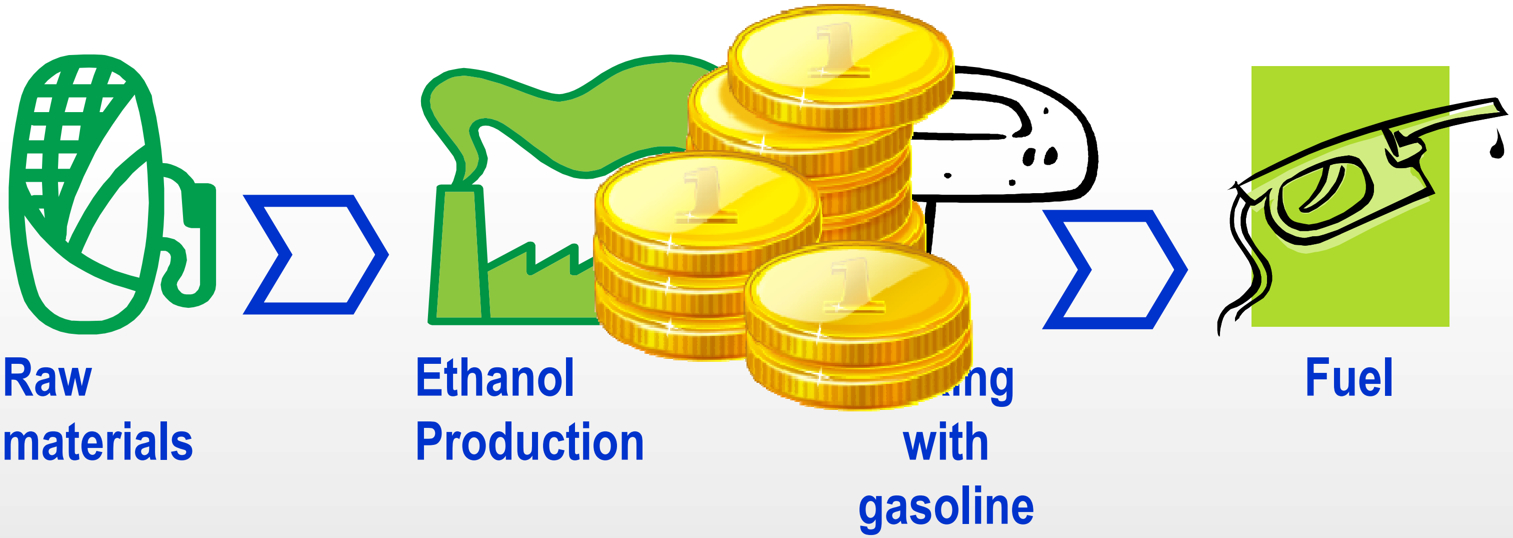
Toluene

Isooctane

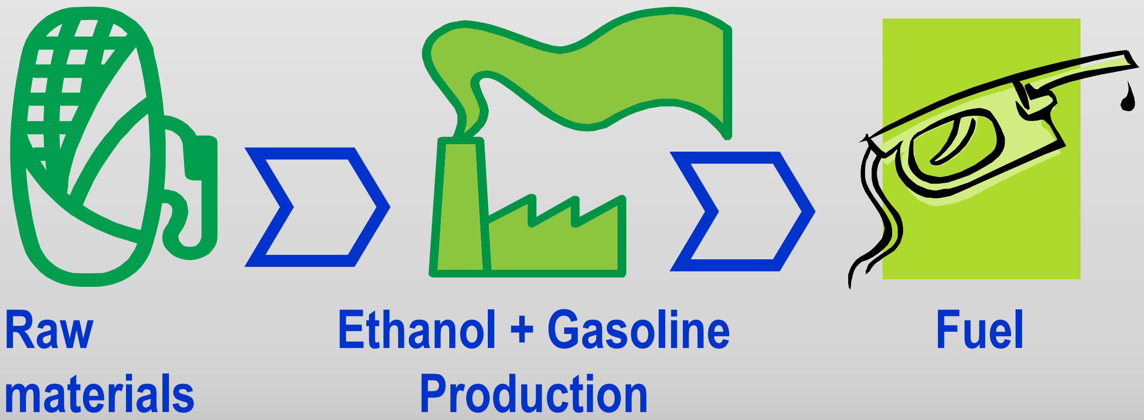
Cyclohexane

Gasoline components

Conventional Process



Proposed Process



INTRODUCTION

Advantages

Cost diminution of:

- Mixing

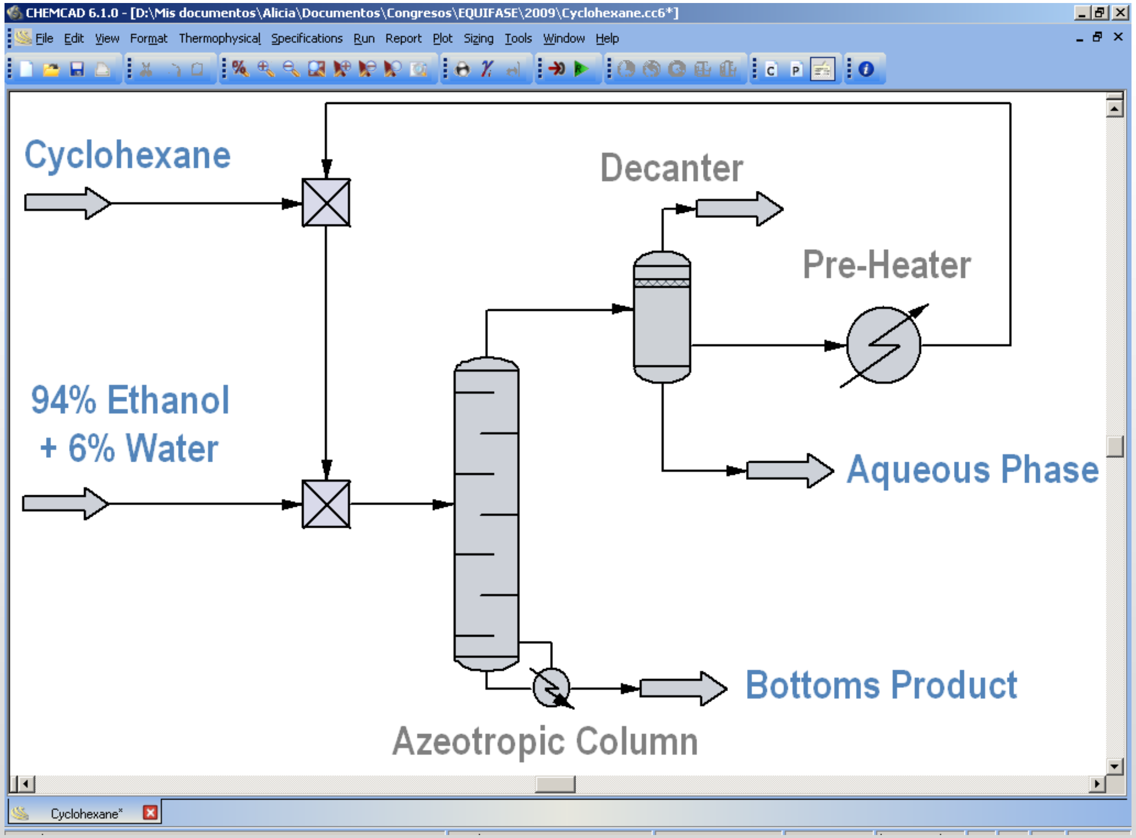
- Transportation

- Storage

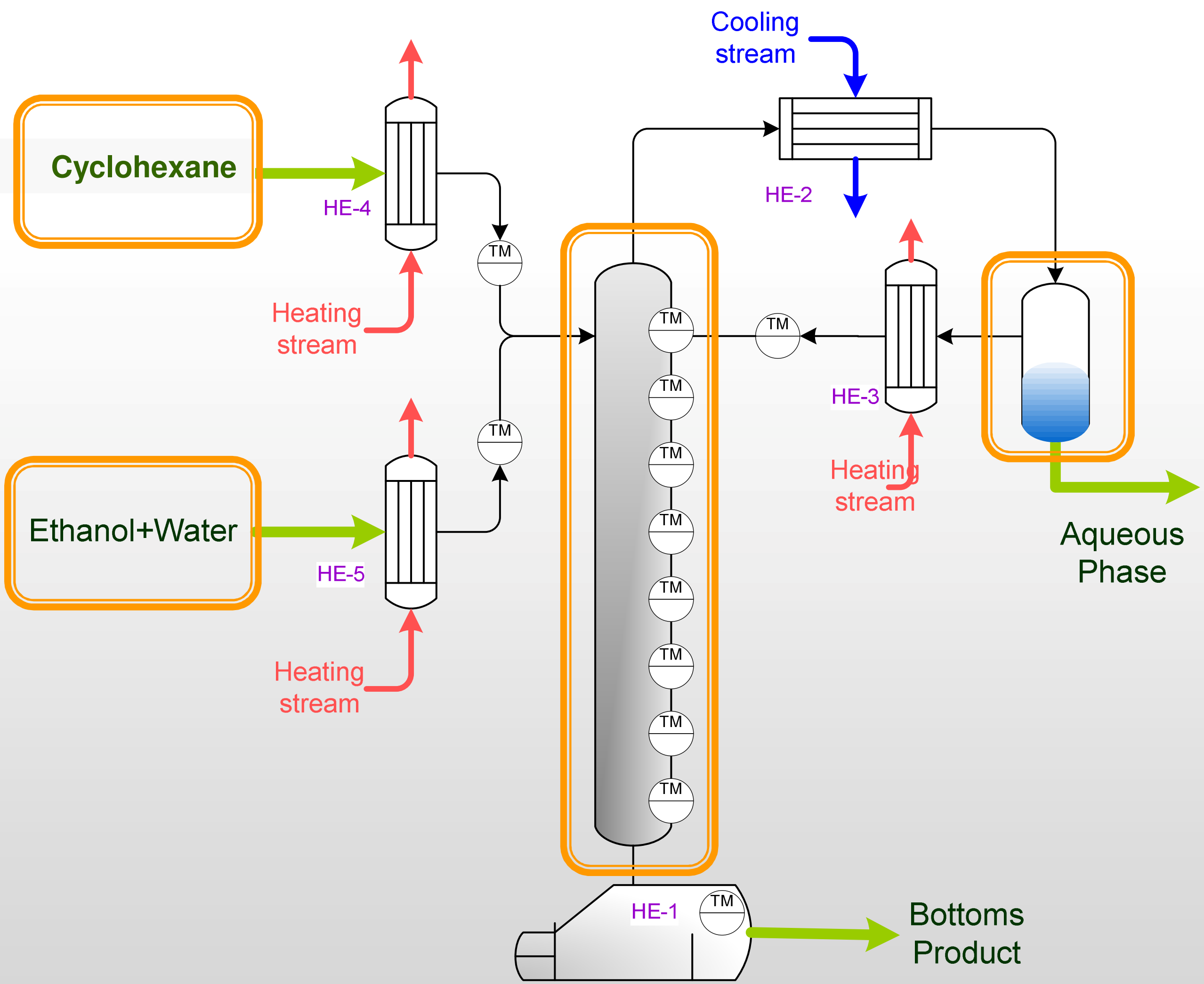
EXPERIMENTAL DESIGN

Study in an experimental semi-pilot plant column

Simulation of the industrial process



Semi-Pilot Plant Column study



Semi-Pilot Plant Column study

Operation Variables

- **Feed 1: pure cyclohexane**. Temperature = 66 ± 1ºC

  Flow rate = 41.00 g/min

- **Feed 2: water + ethanol mixture** (94% wt. of ethanol). Temperature: 63 ±1ºC

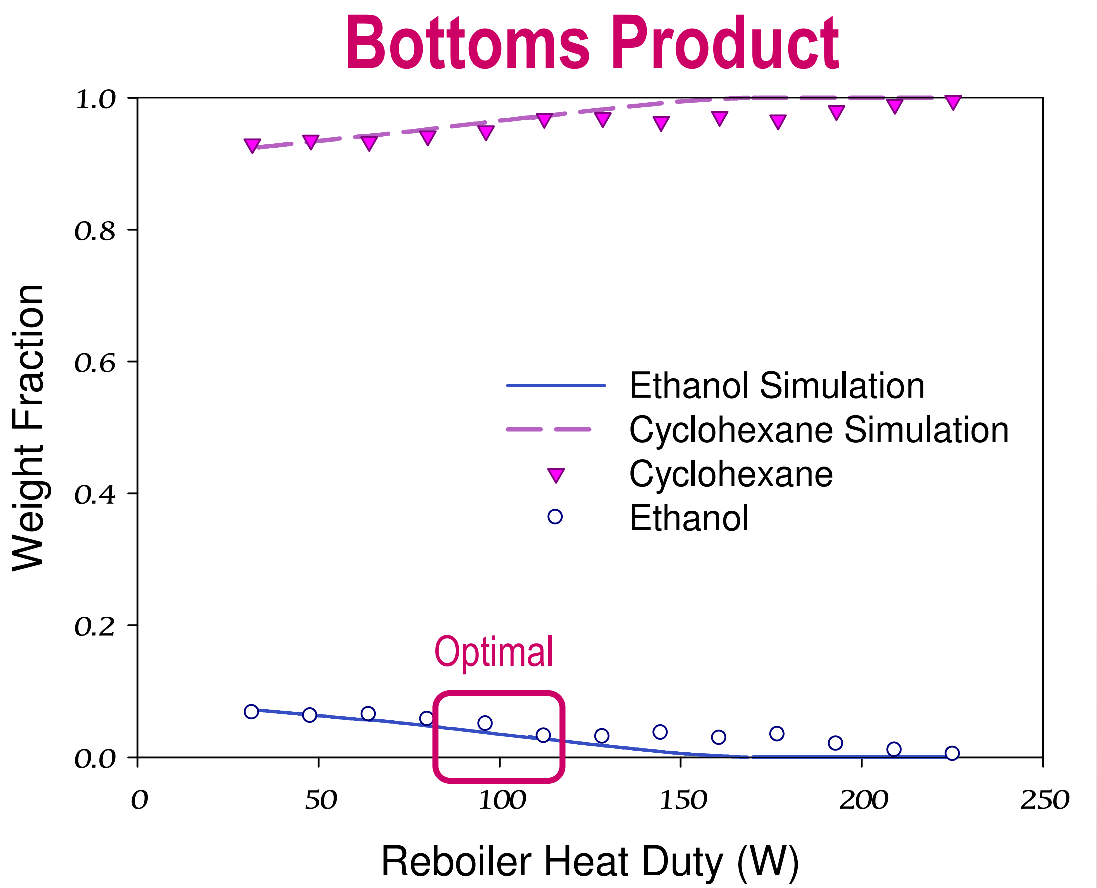
  Flow rate = 4.38 g/min

- **Condenser**: Temperature = 35ºC
- **Heat exchanger 3**: Temperature of the stream leaving HE-3 = 66 ±1ºC

Simulation Variables

- Simulated in **Chemcad 6**
- Rigorous calculation using the **SCDS module** (simultaneous correction method for rigorous fractionation simulation)
- Thermodynamic model: **UNIFAC**

Semi-Pilot Plant Column study

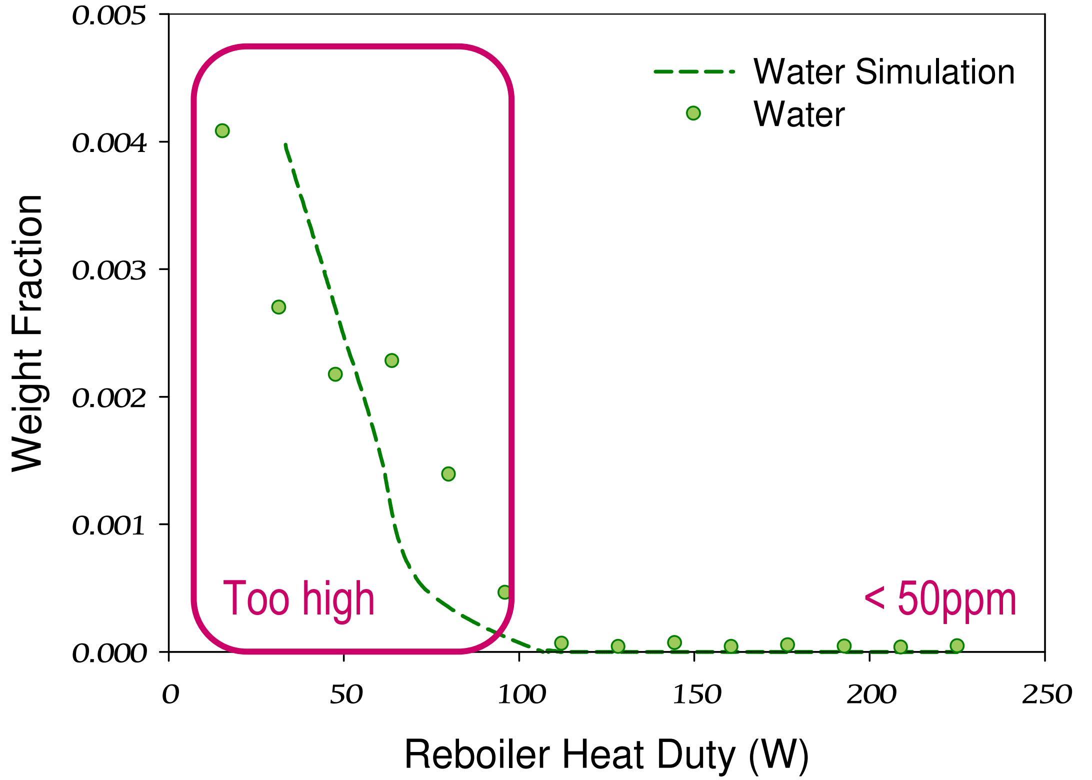


The trends observed in the experimental results resemble their simulated counterparts

- The ethanol concentration depends on the heat duty
- Only values ranging from 80-100 W permit ethanol concentrations close to 5 % wt.

Semi-Pilot Plant Column study

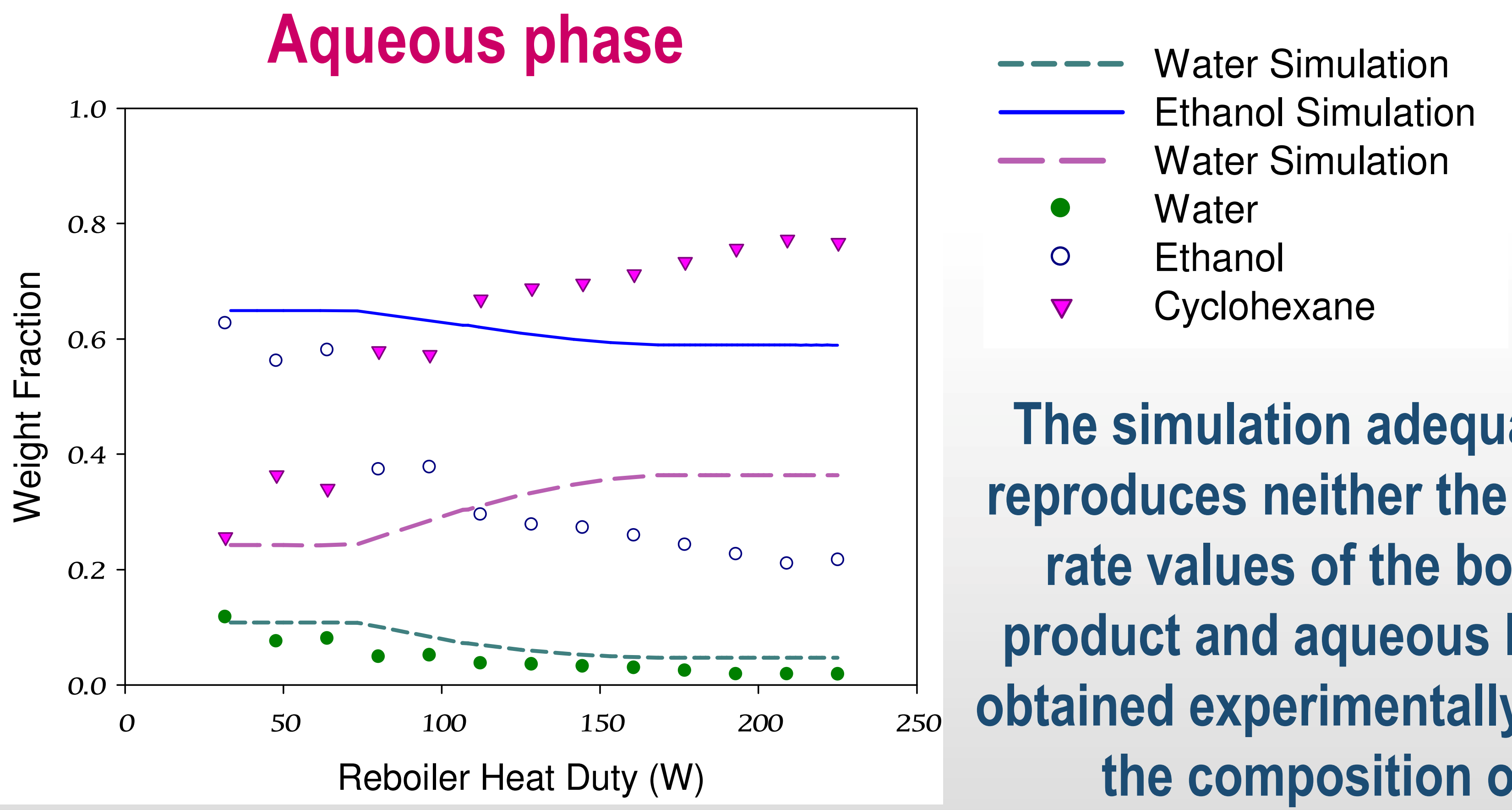
Bottoms Product



The trends observed in the experimental results resemble their simulated counterparts

- The concentration of water in the residue stream does vary considerably with respect to the reboiler heat duty
- As the heat duty increases, the concentration of the water gradually decreases, reaching values lower than 50 ppm.

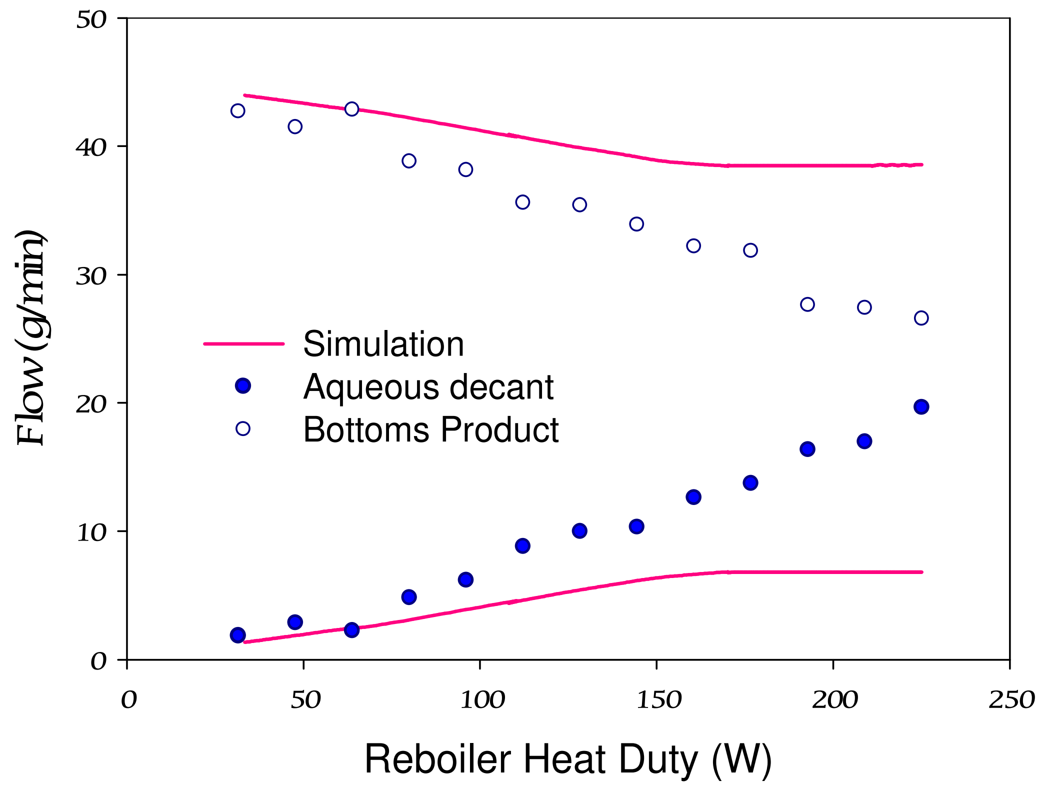
Semi-Pilot Plant Column study



The simulation adequately reproduces neither the flow rate values of the bottom product and aqueous layer obtained experimentally nor the composition of the streams

- The composition of the aqueous layer is also dependent on the heat duty
- The composition tends to approach that of the plait point of the system.

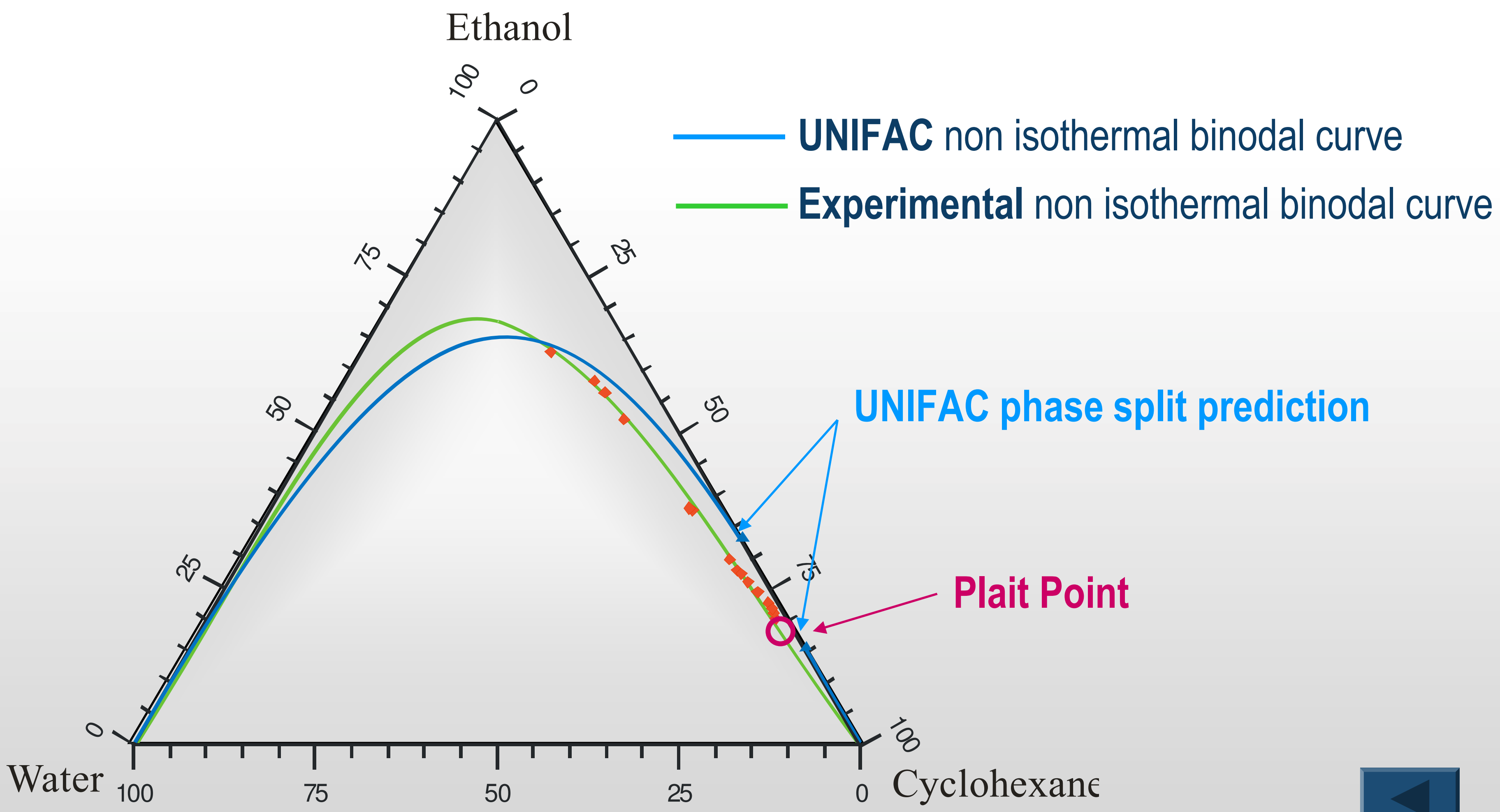
Flows



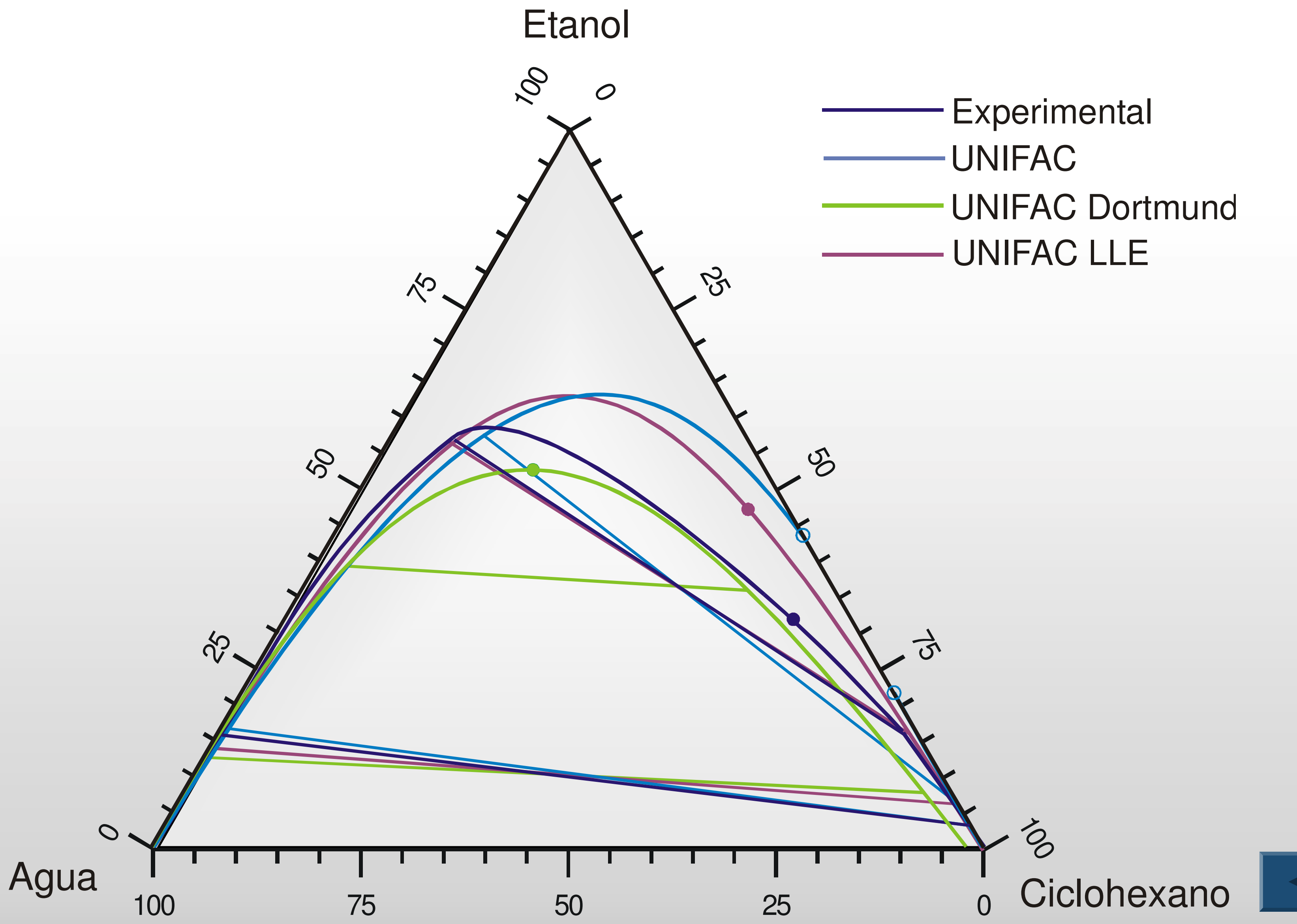
The simulation adequately reproduces neither the flow rate values of the bottom product and aqueous layer obtained experimentally nor the composition of the streams

- The flow rate of the residue is always higher than that of the aqueous layer
- Both flow rates become more similar when the reboiler heat duty increases.

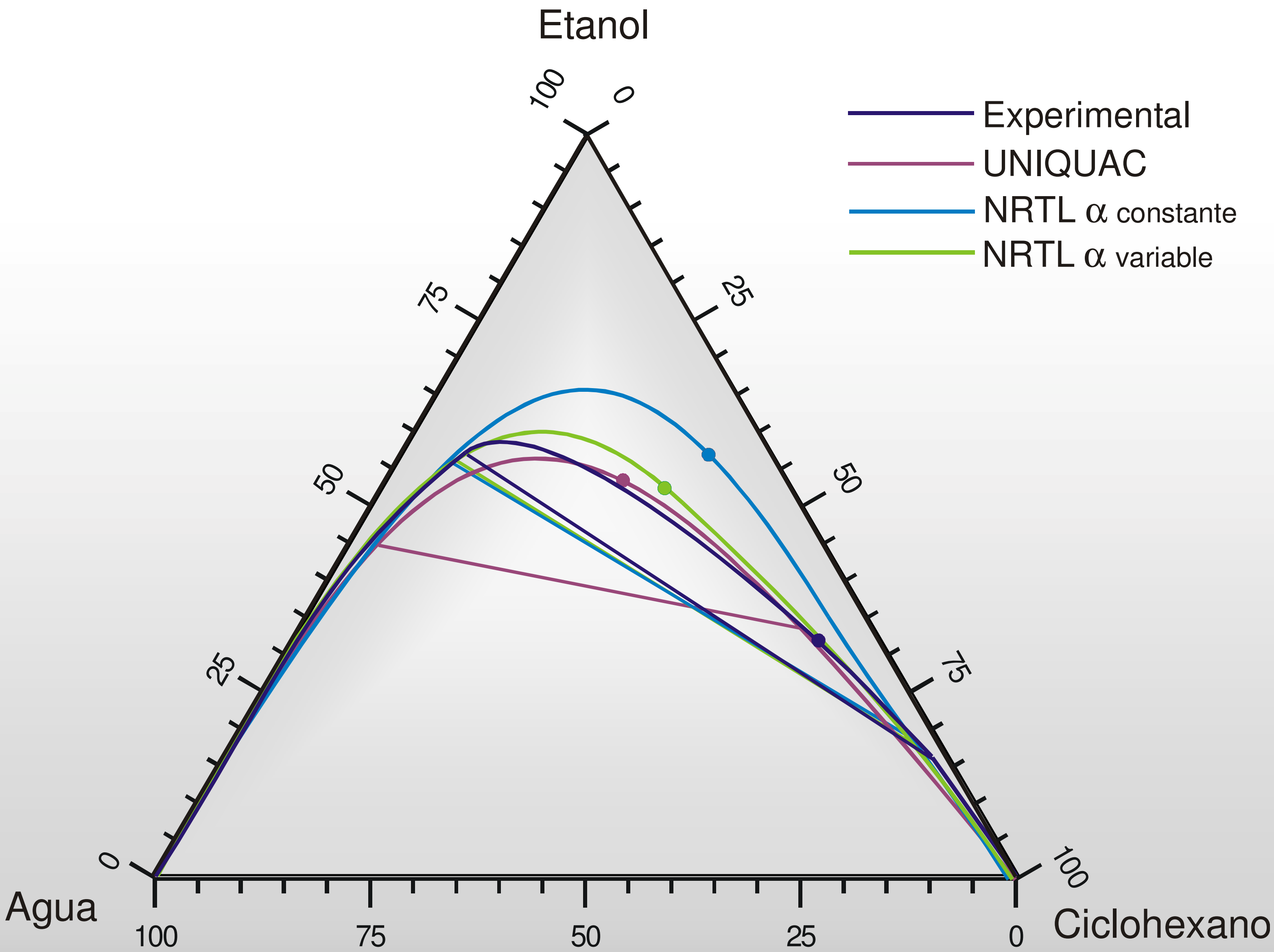
Semi-Pilot Plant Column study



Semi-Pilot Plant Column study



Semi-Pilot Plant Column study



CONCLUSIONS

- It is possible, through azeotropic distillation, to obtain a **mixture of cyclohexane + ethanol with concentrations of water lower than 50 ppm** without the need to distill absolute ethanol beforehand. Afterward, the mixture could be directly employed as a carburant in car engines with no further modifications.
- The most critical parameter of the process is the **reboiler heat duty**. At lower values, this produces a mixture of cyclohexane + ethanol with excessive amounts of water. Whereas, at higher values the azeotropic distillation column does not work properly, since the top stream condenses giving only one liquid phase.
- Significant **differences** in some values are encountered **between experimental and simulated data** which can be attributed to the calculation of the liquid-liquid equilibrium. It is therefore necessary to improve the correlation of the experimental equilibrium data for determined regions of the ternary system diagram.

The production of dry mixture of ethanol + cyclohexane seems to be technically and economically viable